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NASA Contractor Report 165534

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PRECURSORS IN HYDROCARBON FUELS**

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**(NASA-CR-165534) OXIDATION AND FORMATION OF
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Final Report (SRI International Corp., Menlo
Park, Calif.) 26 p HC A03/MF A01 CSCI 21D**

N 82-18402

G3/28 09128
Unclass

January 1982

Prepared for

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract NAS3-22510**



**OXIDATION AND FORMATION OF DEPOSIT PRECURSORS
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The object of this research is to determine the mechanism of deposit formation in hydrocarbon fuels, and thus to predict and to prevent deposit formation.¹ The deposits cause clogged filters and hot fuel lines. Our premise is that such deposits, insoluble in hydrocarbons, arise from further condensation of deposit precursors.² The precursors are the oxidation products of the fuels and condensation products of these, formed in stepwise reactions. When their molecular weights and oxygen contents become high enough, they precipitate from solution,³ either on long storage or quick heating. The problems are: what oxidation products are most likely to condense; is the condensation a radical or a nonradical reaction, or both; what fuels or fuel components are most likely to form precursors; and how can the reactions be prevented?

This paper deals with applying field ionization mass spectrometry (FIMS) to solve these problems. We started with a No. 2 home heating oil ("Fuel C") to represent an unstable jet turbine fuel, then used n-dodecane as a simple and common fuel component. In both approaches, we encountered difficulties but also made substantial progress.

EXPERIMENTAL

One gallon of Fuel C was supplied by the Lewis Laboratory of the National Aeronautics and Space Administration. It was brown and contained so much material of high molecular weight and low solubility that

following the development of additional precursors was impractical. Therefore, 176g of the fuel was distilled at 2.3 kPa (17 torr) in a Claisen flask with a Vigreux neck. The distillate, collected at 54 to 203°C, was pale yellow; 4.14 g of a dark mixture of liquid and solid residue was obtained. Aliquots of the distillate, about 10 mL, were oxidized by shaking them with air in 100-mL flasks in a 130° bath. Gas samples of 70 µL were withdrawn through a septum and analyzed for O₂/N₂ by gas chromatography on a 183 x 0.32 cm stainless steel column at 0°C and 30-mL per minute He flow rate. The column was packed with 13X molecular sieve.

"Pure" 99% n-dodecane was obtained from the Phillips Chemical Company and distilled at 2.3 kPa (17 torr). The first and last tenths were rejected.

A 25.4-cm-radius 90° magnetic sector mass spectrometer was used to obtain the complete molecular weight profile of the fuel samples. This mass spectrometer is equipped with a volcano-style field ionization source and an all-glass batch inlet system. It routinely achieves a sensitivity of 2×10^{-6} ions/molecule and may be connected to a PDP 11/10 computer system program to acquire, average, analyze, and plot mass spectral data.

Molecular weight profiles are obtained by injecting a 5-µL sample of the fuel through a septum into the evacuated 0.5-L glass expansion

bulb of the batch inlet system. The entire fuel sample vaporizes immediately and the mixture of gaseous fuel molecules enters the field ionization source through an 80- μ m-diameter glass leak. Field ionization of this mixture produces molecular ions from each fuel component. The resulting field ionization mass spectrum is therefore a molecular weight profile of the fuel sample. The FIMS/computer system's sensitivity and precision is such that substances which are 1% of the fuel sample can be quantitated with an accuracy of better than $\pm 5\%$.

A second field ionization mass spectrometer system was used to analyze deposit precursors. This is a 25.4-cm-radius, 60° magnetic sector mass spectrometer equipped with SRI's activated foil field ionization source. This mass spectrometer routinely achieves a sensitivity of 2×10^{-7} ion/molecule and has a maximum mass range of 4,000, but with a maximum mass resolution of 1200. It may also be interfaced to the PDP 11/10 computer system, although the mass spectral data system is limited to an upper mass of 850.

Fuel C samples were analyzed for deposit precursors using vacuum evaporation preconcentration. A 0.5-mL fuel sample was spiked with an internal standard, 10 micrograms of decacyclene. The sample was then vacuum-evaporated to less than 100 μ L. A five- μ L sample of the concentrate was placed in a standard mass spectrometer sample holder in the solids probe of the mass spectrometer. The probe was cooled to -50°C , introduced into the mass spectrometer vacuum system, and then warmed to 30°C with continuous pumping to remove most of the remaining volatile components. The probe was then mated with the ion source. The field ionization spectrum of the residue, including deposit precursors and

decacyclene internal standard, was collected with the PDP 11/10 computer system. The resulting FIMS spectra, therefore, represent the composition of the least volatile components of the fuel sample. Any low volatility impurities in the fuel will also appear in the FIMS spectrum of this residue. Because the internal standard (decacyclene) was spiked at the level of 20 ppm (by weight), the concentration of individual deposit precursors is calculated by comparing their intensities in the FI spectrum with the intensity of the peak from the decacyclene standard.

The procedure for analyzing samples of oxidized dodecane was the same as for Fuel C, except that the internal standard was perylene (molecular weight 252). In general, it was not possible to remove all of the dodecane because its volatility was too close to that of the dodecane oxidation products.

RESULTS

Fuel C. Table 1 summarizes the results of an oxidation of distilled Fuel C; they show steady increases in rate of oxygen absorption (auto-catalysis) and in concentration of less volatile material.

Table 1

RESULTS OF THE OXIDATION OF VACUUM-DISTILLED FUEL C

Parameter	Sample			
	B34501	A34502	A34503	A34504
Time at 130°C (min.)	0	255	430	701
O ₂ consumed (mmol/liter)	0	6.55	13.1	32.2
Per minute ^a x 10 ²		2.6	3.7	7.0
Deposit Precursor Properties				
Concentration (ppm) ^b	74	132	2540	2600
Number Av. Mol. Wt., \bar{M}_n	435	388	355	318
Weight Av. Mol. Wt., \bar{M}_w	496	440	419	381

^a During preceding interval

^b Based on total materials found by FIMS

Figure 1 shows the molecular weight profile of distilled, but unoxidized, Fuel C. The abscissa corresponds to the mass number of the ions in the mass spectrograph. The full ordinate is 10% of the sum of all the ion intensities. Thus the 156 mass unit bar means that 8.8% of the fuel concentrate consists of material of molecular weight 156. All the principal components have even mass numbers, as will all compounds of C, H, and O (but not N). However, 1.1% of natural C is ^{13}C , and so for any 12-carbon compound, about 13% of the molecules will contain one ^{13}C and have a molecular weight that is higher by one unit. Therefore, all the major peaks will have an obvious satellite with mass number one unit greater. Thus the 156 peak in Figure 1 is accompanied by a 157 peak that is 13% as high.

Figure 1 shows several series of major peaks that differ by 14 mass units, corresponding to homologous series differing by one or more CH_2 units. The 106 to 134 series corresponds to alkylbenzenes with two to four carbon atoms in side chains. The 142 to 198 series corresponds to paraffins with 10 to 14 C atoms, with unknown branching. Peaks at 168 to 224 correspond to hydrocarbons with one ring or double bond. Other peaks correspond to compounds with additional rings or double bonds. Similar molecular weight profiles of oxidized Fuel C are not useful: at low conversion, the concentration of each hydrocarbon does not change much and each gives small quantities of several oxidation products, with opportunities for compounds with different C:H:O ratios to have the same mass number.

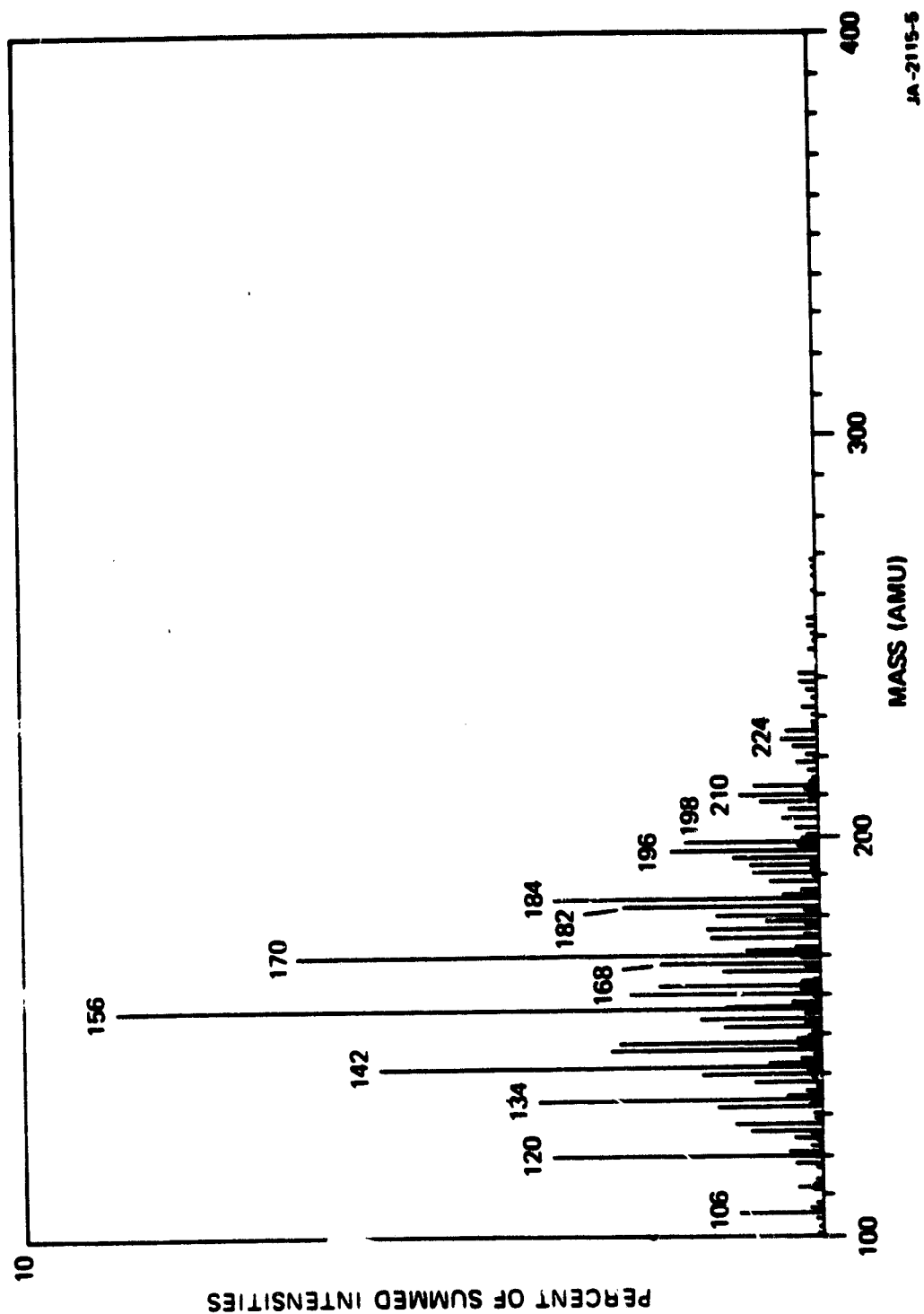
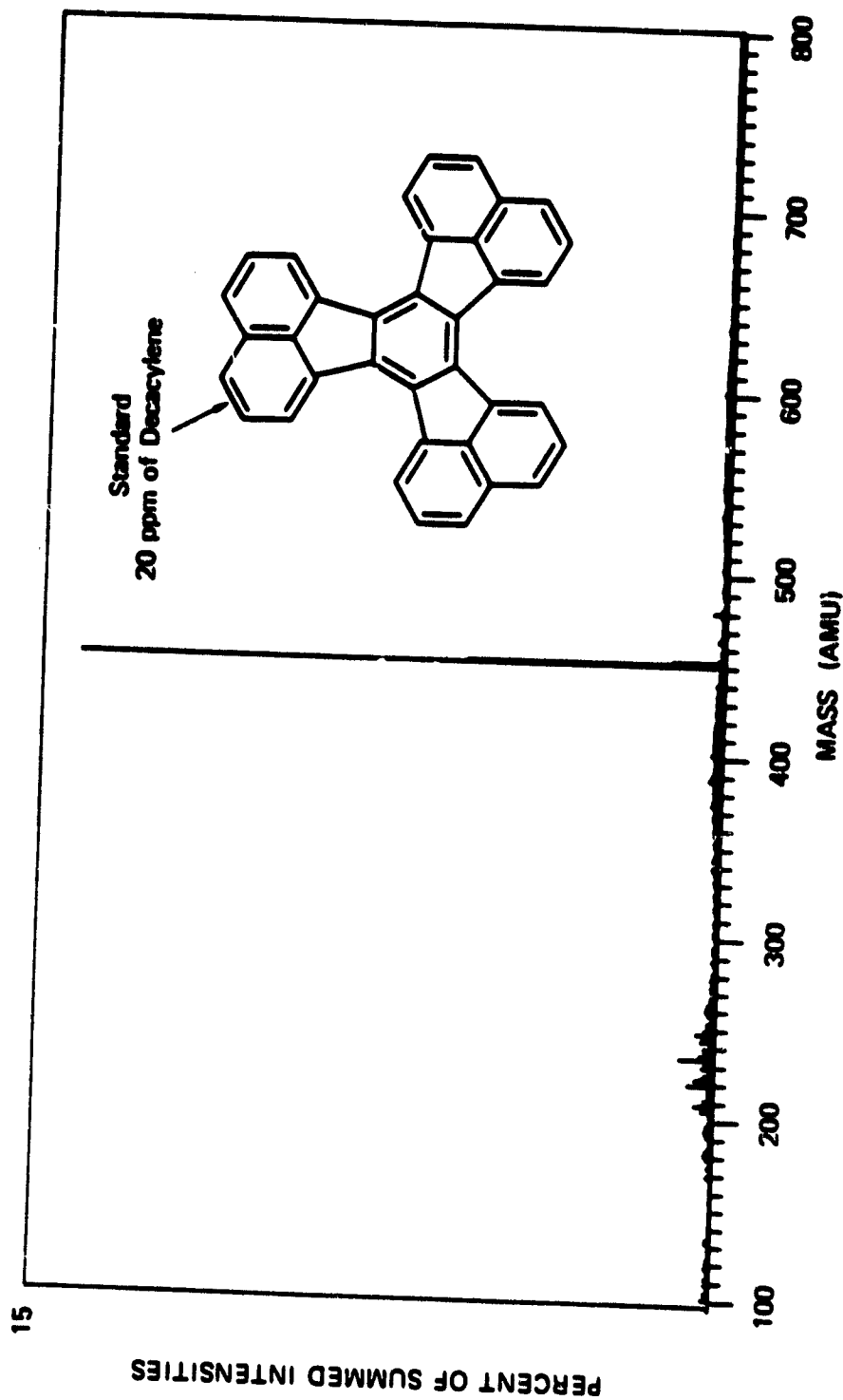


FIGURE 1 MOLECULAR WEIGHT PROFILE OF THE DISTILLED SAMPLE (OF FUEL C: 1-BuO₂ was added to a concentration of 0.01 M, but the fuel was not oxidized).

Figures 2 to 5 summarize FIMS data after the four periods indicated in Table 1. Each sample was spiked with 20 ppm of decacyclene ($C_{36}H_{18}$, molecular weight 450, structure in Figure 2). The ordinate and the numbers in the upper left corners of the figures are the percentages of the summed ion intensities. Figure 2 shows the distilled but unoxidized Fuel C. Traces of the higher molecular weight products can be seen in Figure 1, but the spectrum brings out the minute traces of a great number of compounds swept over in the distillation or formed between distillation and taking the spectrum.

Figures 3 to 5 show the FIMS after the three oxidation periods in Table 1. Most of the material of molecular weight ~ 250 corresponds to incorporation of one to four atoms of oxygen into fuel molecules (precursor monomers), retained because they are much less volatile than the fuel. Most of the material with molecular weights between 300 and 450 represents combinations of monomer precursors. Material of intermediate molecular weight presumably represents condensation of monomer precursors and their fragments formed by cleavage of alkoxy radicals. Figures 2 and 3 show that the development of monomer precursors and dimer precursors, like the rate of oxygen absorption, is autocatalytic. Development of trimers can also be seen.

During the oxidation period that ended with the product in Figure 5, the solution became lighter and a dark brown precipitate formed on the reactor walls. During this period, the concentration of precursor monomers increased sharply (these may be the ones that don't condense easily); and the concentrations of dimers and trimers appear to decrease perceptibly (compared with the decacyclene standard), perhaps because they have separated from the fuel mixture.



JA-2115-1A

FIGURE 2 FI MASS SPECTRUM OF THE DEPOSIT PRECURSORS ISOLATED FROM A SAMPLE OF VACUUM-DISTILLED, UNOXIDIZED FUEL C

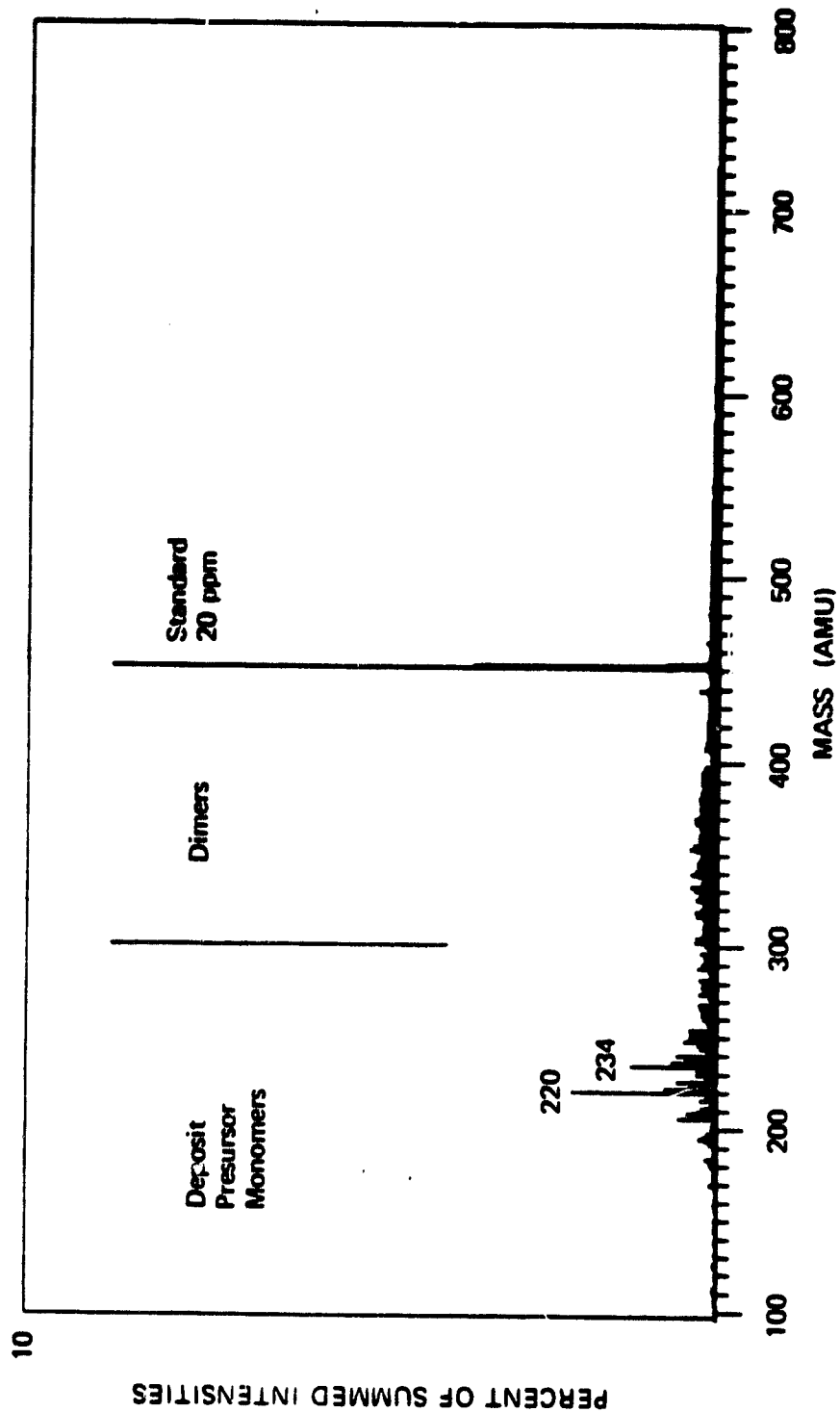


FIGURE 3 FI MASS SPECTRUM OF THE DEPOSIT PRECURSORS FORMED IN FUEL C AFTER
OXIDATION FOR 255 MINUTES AT 130°C

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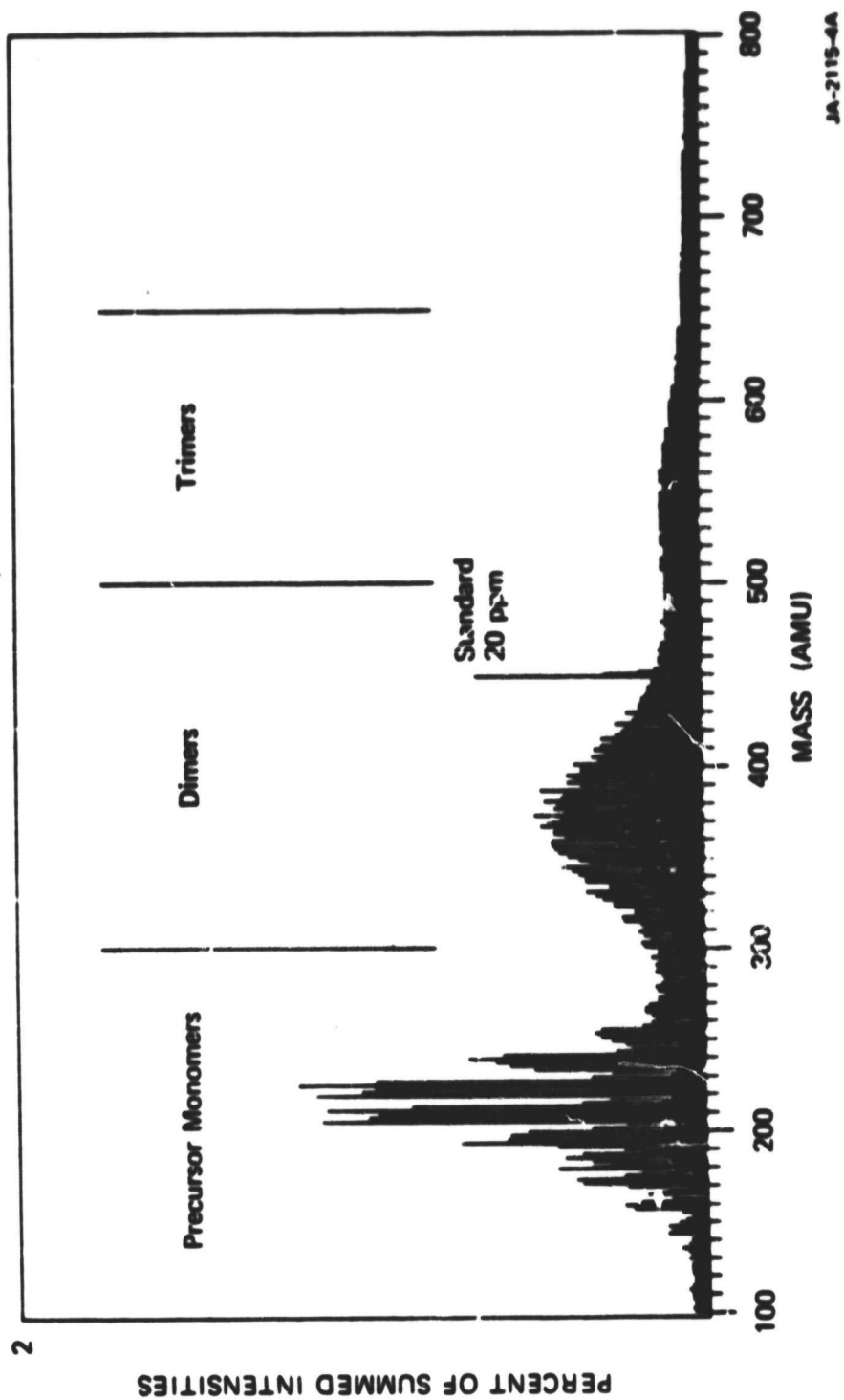
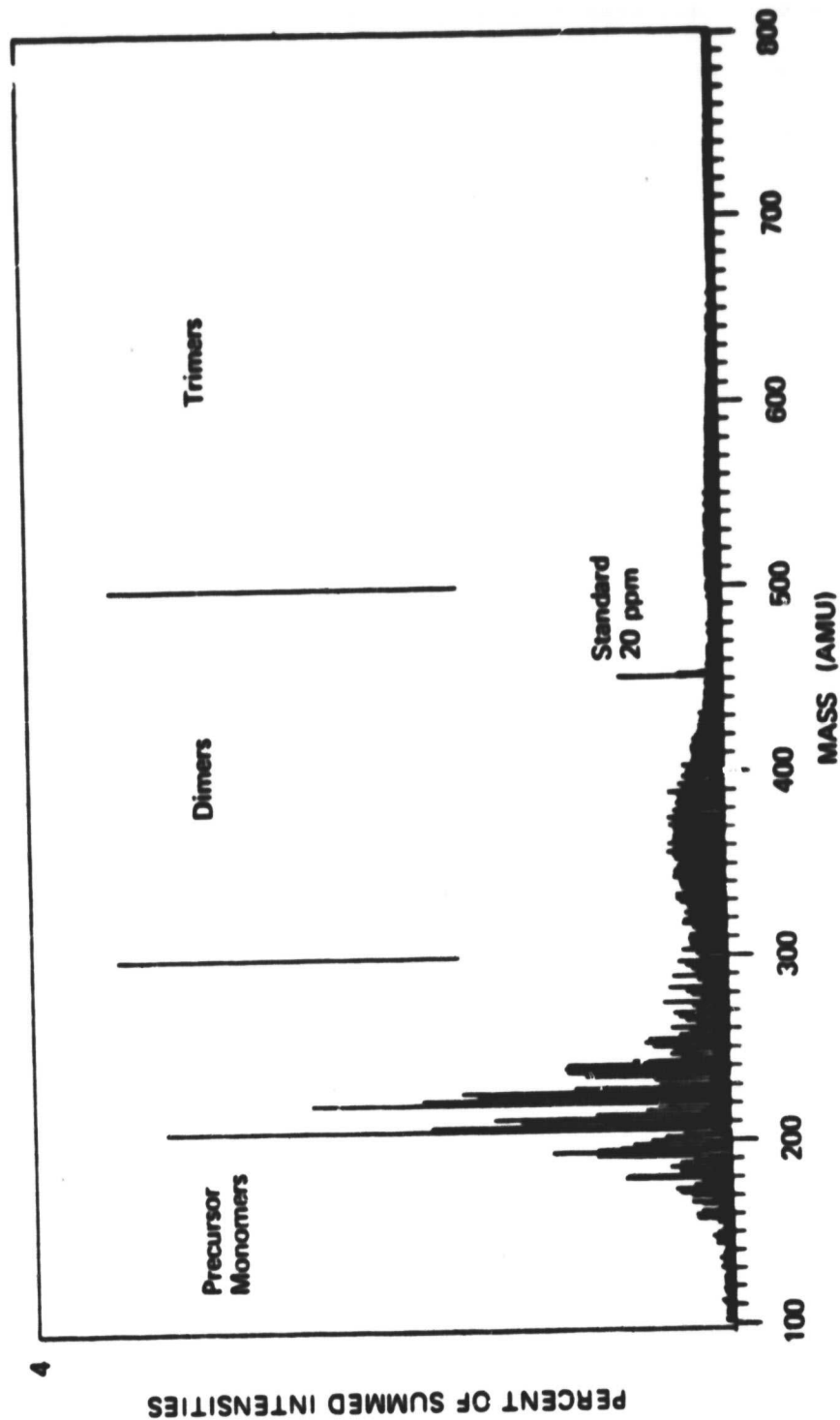


FIGURE 4 FI MASS SPECTRUM OF THE DEPOSIT PRECURSORS FORMED IN FUEL C AFTER
OXIDATION FOR 430 MINUTES AT 130°C



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FIGURE 5 FI MASS SPECTRUM OF THE DEPOSIT PRECURSORS REMAINING IN FUEL C AFTER
OXIDATION FOR 701 MINUTES AT 130°C

The precipitate that formed, after washing with hexane and drying, weighed about 3 mg/g of initial fuel. Acetone extraction of this residue gave 0.137 mg of extract/g initial fuel; its \bar{M}_n in N-dimethyl formamide was ~600. It therefore appears that the deposits precipitate more because of their oxygen and heteroatom contents than because of their high molecular weights.

Although the research described above provides excellent evidence for the deposit formation by stepwise condensation of deposit precursors, the data give us little indication of the chemical structures or mechanisms involved. However, there is an indication with Fuel C of a problem that becomes much more obvious with n-dodecane. Comparing Figures 2 through 5 with Figure 1 shows that the oxidized products have higher proportions of materials with odd mass numbers (in the spaces between the peaks with even mass numbers). Odd mass numbers in C, H, and O compounds, except those due to ^{13}C , mean that fragmentation of parent molecules has occurred in the FIMS.

n-Dodecane

To eliminate the multicomponent problem with Fuel C, we investigated the oxidation of n-dodecane. Two sets of oxidations were carried out. In the first set, a 30.6 mmol aliquot was oxidized for 12 hours at 130°C in a sealed tube containing air; 0.541 mmoles of oxygen was absorbed, 1.76 mol % on the dodecane used. Part of this product was used directly in the FIMS and part was first heated for one hour at 180°C in a sealed, evacuated tube to destroy peroxides. Known 3-dodecanol and 2-dodecanone were also investigated. Because the extents of evaporation varied before taking FIMS data, the absolute

concentrations of products vary considerably in the three spectra. Dodecane (mass number 170 and its satellite at 171) predominated in the FIMS concentrates but are irrelevant and neglected in this discussion. Table 2 therefore lists the 12 strongest other peaks for each spectrum in order of their relative intensities.

Table 2 shows that with the untreated oxidation product, the four strongest peaks, and 7 of the 12 strongest, have odd mass numbers. These must represent molecule fragments, and so we examined the FIMS of known 3-dodecanol and 2-dodecanone. The dodecanol shows little of the parent ion (186), but it decomposes in the FIMS to give six principal significant products: 50 mol % is dodecyl (169 by loss of HO); 20% is decyloxy (157 by loss of ethyl); 18% is dodecene (168 by loss of water); 13% is dodecanone (184 by loss of H₂); 5% is dodecyloxy (185 by loss of H); and 4% is undecyloxy (171 by loss of methyl). The second and last products are probably specific for 3-dodecanol, leaving dodecyl as the principal product from mixed dodecanols. 2-Dodecanone is relatively stable. The parent peak (184) and its ¹³C satellite (185) comprise >90% of the observed ions.

In the oxidation products, the 182 and 183 peaks are probably fragments from dodecyl hydroperoxides because they disappear or decrease upon heating and are replaced by alcohol-derived peaks at 169 and 185. The 184 parent peak for dodecanone is little changed on heating. The 169 peak is associated with both alcohol and hydroperoxide but must come only from alcohol in the heated product. The new 203 and 373 peaks in the heated sample probably arise from peroxides with >2 oxygen atoms or two dodecane residues. The 12-carbon products with two and

TABLE 2

PRINCIPAL IONS FROM 3-DODECANOL, 2-DODECANONE, AND OXIDATION PRODUCTS OF n-DODECANE										
NO OXIDATION			FIRST OXIDATION		SECOND OXIDATION					THIRD OXIDATION
RANKING	3-DO- DECANOL	2-DO- DECANONE	UNTREATED	HEATED TO 180°	UNTREATED	TREATED			BENZO- YLATED	Ph ₃ P ^a
						VIEWED J 180°	WITH KI + AcOH	KI + HEATED		
1	169	184	183	169	183	169	182	182	290 ^d	169
2	157 ^a	185	169	185	169	183	183	264 ^c	98 ^d	184
3	168	182	199	199	199	184	169 ^b	296 ^c	184	168
4	131	122	165	203	184	185	311 ^b	183 ^c	182	182
5	184	183	184	184	182	203	370 ^b	328 ^b	198	185
6	185	150	217	201	185	198	256 ^b	256 ^b	194 ^d	157
7	171 ^a	155	182	217	197	57	184	184	370 ^d	143
8	373	170	201	183	198	182	185	169 ^c	189 ^d	129
9	186	186	216	198	217	199	198	256 ^c	203 ^d	
10	183	136	197	373	370	85	297 ^b	266 ^c	302 ^d	
11	182	156	198	159	196	71	283 ^b	213 ^c	185	
12	198	108	370	186	99	58	371 ^b	196	183	

Suggested identifications of ions above.

57	C ₄ H ₉	182	dodecenone	256 ^{bc}	ROH
58	C ₆ H ₁₀	183	↓	264 ^c	2 { rings
71	C ₈ H ₁₁	184	dodecanone	266 ^c	1 { or C=C
85	C ₈ H ₁₃	185	dodecyl-O	290 ^d	dodecyl-OBz
98	Heptane	186	dodecanol	291 ^d	
99	C ₇ H ₁₅	189		296 ^c	RH
129	C ₈ H ₁₇ O			297 ^{bc}	RO
131	C ₈ H ₁₇ OH ₂	194	C ₁₂ diketone - 4H	310	ketone
143	C ₈ H ₁₉ O	196			
157	C ₁₀ H ₂₁ O ^a	197	↓	311 ^b	RO
159	C ₁₀ H ₂₁ OH ₂ or C ₈ H ₁₉ O ₂	198	C ₁₂ diketone	328 ^c	ArH - 2H
		199	↓	370 ^{d,h}	See
168	dodecene ^a	201	↓	371 ^c	text
169	dodecyl	203	dodecanediol + H	371	dimer(OH)(=O)O
171	C ₁₁ H ₂₃ O ^a	213	dodecanetriol + H		
172	C ₁₁ H ₂₃ OH ^d	216	↓		
		217	dodecanetriol + H		
174 ^d	ArH - 2H				
175 ^d	Ar				

^a From specific cleavages of 3-dodecanol.

^b Specific for KI.

^c Appear or persist after heating KI sample.

^d Peculiar to benzylation product. M/Z = 226, 227, Bz₂O, were the strongest peaks but 122, BzOH, the next strongest, and 104, benzoyl, are excluded from rankings.

^e In 20 h at 130°, 7.25g, 42.6 mmole of n-dodecane absorbed 0.667 mmol O₂, 1.57 mol % . The hydroperoxide content of an aliquot corresponded to 24.8% of the O₂ absorbed. The remainder of the product was then treated with 20% excess triphenylphosphine for 6 hours at room temperature and then distilled at 1.7 mmPa (13 torr) to remove phosphine and its oxide. This sample should not include high-boiling products.

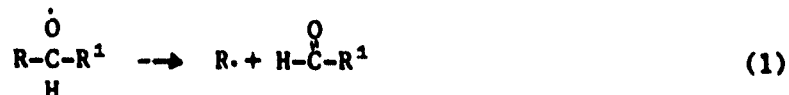
three oxygen atoms are notably and expectedly stronger in the oxidation products than in 3-dodecanol. Mass numbers 194 to 203 and 213 to 217 are closely related products corresponding to gain or loss of H atoms by alcohols and ketones; the borderline between the parent compounds is fuzzy. Volatility considerations must favor the higher oxygen compounds in the data observed for 12-carbon products.

Most of the complications in the first, third, and fourth columns of data in Table 2 are associated with fragmentations of alcohols (and possibly also of hydroperoxides). An effort was made to avoid fragmentation by acetylating, methylating, or benzoylating pure higher alcohols. 5-Dodecyl acetate gave mostly dodecene and then unidentified or cleavage products. 6-Tridecyl methyl ether appeared to decompose mostly to tridecanone and methane, but also to tridecene. 6-Tridecyl benzoate gave mostly the parent peak.

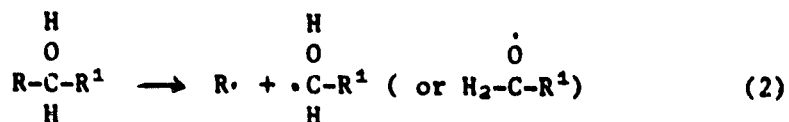
The second set of experiments on the oxidation of dodecane is also summarized in Table 2. n-Dodecane was oxidized for 22.3 hours at 130°C; 120.6 mmol of dodecane absorbed 1.35 mmol of oxygen, 1.12 mol %. Thus less reaction occurred in a longer time, presumably because of oxygen depletion. Part of the product was subjected to FIMS directly; part was heated for one hour at 180°C in the absence of oxygen to destroy peroxides. A major portion was treated with aqueous KI and acetic acid to decompose peroxides. The liberated iodine was titrated with sodium thiosulfate. The hydroperoxide content corresponded to 34% of the oxygen absorbed. Part of the KI-treated products was then

heated for one hour at 180° in the absence of air and another was benzoylated with 20% excess benzoyl chloride in pyridine.*

From Table 2, the results with the heated and unheated oxidation products are qualitatively similar. The principal difference is the appearance on heating of the second set of a homologous series at mass numbers 57 to 99, corresponding to butyl and heptyl ions, and the displacement of the 196, 197, and 217 peaks from the 12 most prominent products after heating. The radicals at mass numbers 57 to 99 should arise from cleavage in the FIMS of hydroperoxides in the unheated oxidation products,



or from alcohols in either the heated or unheated products:



The KI treatment of the oxidation products was expected to decompose hydroperoxides to alcohols without forming free radicals or by-products. However, the 182 dodecenone peak is stronger than in any previous experiment: it may come from either dodecanone or dodecanol. New strong peaks appear at 256, 283, 297, 311, and 370; all but 256 and 297 weaken or disappear when the KI product is heated. These new

* After washing out the pyridine, the product was shaken with saturated aqueous K₂CO₃ for several hours to reduce the concentrations of acid chloride and anhydride and dried with anhydrous K₂CO₃. Even so, the small amounts of benzoic acid and anhydride remaining appeared as major products in the FIMS. The 104 benzoyl peak and several metastable peaks from Bz₂O₂ are omitted from Table 2.

peaks may represent significant byproducts of the KI reaction, but more probably, they represent FIMS-exaggerated traces.

In comparison with the KI reduction, the triphenylphosphine reduction gives more products that are more typical of dodecanols (168, 169, 185) and thus may be a cleaner reduction. However, the absence of peaks above 190 in the triphenylphosphine products is probably due to distillation before FIMS (note e, Table 2).

The 370-371 peaks appear in several mixtures in Table 2 and are prominent in all the mixtures in Table 3, except in the KI + heat group. They do not survive heating after KI treatment, but they survive benzoylation and so are not associated with hydroxyl groups, even though mass number 370 corresponds to a dimer glycol. The 370-371 products may come from some combination in a dimer of carbonyl and ether groups that produces these peaks in FIMS.

The heated products are similar to the KI products, containing considerable material of mass numbers 169, 182-185, and 198-199. However, the heated products contain more low mass number fragments and the KI products give more ions with mass number >256. Of the six new mass numbers that appear in the KI sample, the 256 peak persists after heating but five weaken or disappear (283, 297, 311, 370, 371) and some new ones appear. Thus, substantial changes occur upon heating the KI product, even though there are no peroxides left, and hence nonradical reactions as well as radical reactions may lead to polymeric precursors.

Interposing the KI treatment before heating makes the dodecenone peak (182) most important, weakens or eliminates several peaks (57, 58,

71, 85, 185, 199, and 201) and forms several new ones, mostly >250.

The benzoylated KI-treated product contains more dodecyl benzoate (290) than anything else, and establishes hydroperoxide and alcohol as the major primary products. The 168 and 169 peaks show that benzoylation of alcohol was essentially complete. The 182, 184, and 185 peaks that persist probably come from dodecanones, but in the KI-treated product, they and the 183 peak may also come from dodecanols (cf. Table 2).

Table 3 shows the relative ion concentrations from dimeric products. The most prominent appear in Table 2. These products appear in groups corresponding to the dimer (338) and products containing 1, 2, and 3 additional oxygen atoms (near 354, 370, 386, and maybe 402) minus a few hydrogen atoms for formation of ketones or alkoxy radicals instead of alcohols. Starting at about mass number 399, most of the higher mass numbers must represent two dodecane residues plus oxygen plus additional carbon-containing fragments. No trimeric fragments (506 or above) have been observed, probably because of precipitation or volatility limitations. However, their absence may instead be caused by low yields with dodecane, because trimers were observed with Fuel C.

We now consider the mechanism by which monomers are converted into dimeric products. The simplest condensation of dodecane by heating with a hydroperoxide would be:



The molecular weight of the C_{24} dimer is 338, but none of this was found in the first set of oxidation products. Instead, the C_{24} products found had 2 to 4 oxygen atoms and mass numbers close to 370, 385, and 399.

TABLE 3

**PRINCIPAL IONS FROM OXIDATION PRODUCTS N-DODECANE
OF MASS NUMBER ≥ 337**

<u>RANKING</u>	<u>UNTREATED</u>	<u>HEATED</u>	<u>UNTREATED</u>	<u>HEATED</u>	<u>KI</u>	<u>KI + HEAT</u>
1	370	373	370	337 ^a	370	450 ^b
2	385	385	385	385	371	466
3	399	399	399	399	385	436
4	371	371	371	353	399	366
5	401	355	337	367	337	385
6	386	367	367	371	469	337
7	400	353	369	355	355	340
8	387	337	353	366	353	338
9	383	350	355	370	339	365
10	415	369	450	338	367	399
11	368	374	436	351	338	451
12	369	386	366	369	366	367

Suggested identifications of ions above.

337	- H	364	- 2H	399	$\left. \begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right\} \begin{array}{l} \text{C}_{24}\text{H}_{50} \\ + \\ 4 \text{ or} \\ \text{more} \\ 0 \\ + \\ \text{fragments} \end{array}$
338	Dimer, $\text{C}_{24}\text{H}_{50}$	366	Dimer diketone	400	
339	+ H	367		401	
340		368			
		369		415	
351	Dimer ketone - H	370			
353	Dimer-O	371	Dimer diol + H	436	
355	Dimer OH_2				
		383	- 3H, Ketone	450	
		385	- H	451	
		386	Dimer triol	466	
		387	+ H		
				506	Trimer, $\text{C}_{36}\text{H}_{74}$

^a Would be Number 13 in Table 2.

^b Peak height was $\sim 2/3$ that of the 196 (Table 2).

Thus, the dodecane oxidation products have condensed during oxidation (whatever the mechanism) even though the parent dodecane concentration is 50 times greater than that of the oxidation products. However, the 337 ion, formed by loss of a hydrogen atom from the dimer, is the major product in the heated portion of the second oxidation, although it was not in the unheated portion of the first four oxidations listed in Table 2. Thus, although dodecane is the largest constituent of the oxidation mixtures, it is usually the oxidized dodecanes that condense to dimers.

In the two untreated oxidation products, the four most prominent peaks in Table 3 are identical: they correspond to a dimer plus two or three oxygen atoms and either a fourth oxygen atom or an additional carbon atom. The second oxidation, which may have been depleted in oxygen, tends to contain dimer units with fewer oxygen atoms and more fragments containing additional carbon atoms (436,450).

Comparing the last two columns of Table 3 shows that heating peroxide-free mixtures to 180° formed higher molecular weight compounds. Thus, there is a condensation or coupling reaction that does not depend on hydroperoxides, but probably involves other functional groups.

SUMMARY AND CONCLUSIONS

Our experimental results will now be used to formulate a general picture of deposit formation and plans for further work. Oxygen is required to produce deposits from hydrocarbon fuels, except at pyrolysis temperatures. For a given hydrocarbon, the process goes mainly through monomer oxidation, and coupling of these oxidation products to dimeric products.² All of these are at first soluble² in fuel, but as oxidation and condensation continue, the products become insoluble at molecular weights around 600. The insoluble products formed in storage probably remain soluble in good solvents (e.g., acetone), but when fuel containing soluble deposit precursors is heated, especially with a little oxygen, oxidation and condensation become rapid and precipitates form on the walls. These precipitates may at first be soluble in acetone but eventually become intractable. The oxidations are almost certainly conventional free radical chain reactions; the coupling of monomer units probably involves both a free radical coupling mechanism like Reaction 3, and a nonradical condensation (e.g., aldol⁴), the proportions of which are unknown and probably dependent on fuel composition, temperature, and catalysts. Nitrogen and sulfur compounds concentrate in the precursors and deposits because they are more reactive in oxidation and condensation, and probably less soluble in fuel.⁵ Whether the effects of some very reactive fuel components are stoichiometric or catalytic remains to be determined.

Products and fragments between 190 and 338 (dimer) mass number must contain at least two oxygen atoms. Because peroxide links are

not expected to survive FIMS, most products in this range contain two or more oxygen-functional groups. Their proportion is difficult to estimate with FIMS because of volatility differences, but the work of Jensen et al.⁶ on the liquid-phase oxidation of hexadecane at 120 to 180°C shows that at least a quarter of the hydrocarbon molecules attacked contains two or more oxygen functions. Such products are expected and found to be more reactive than monofunctional compounds in radical-coupling and condensation reactions.

At 130°C in air, dodecane oxidizes much faster than Fuel C; it absorbs about 13.2 mmol of oxygen/mol fuel in 10 hours, compared with about 3.82 mmol for Fuel C in 20 hours. Fuel C oxidizes at a constant rate while the rate for dodecane is autocatalytic (very rapid after a slow start). However, by FIMS and observed deposit formation, dodecane produces fewer precursors and no visible deposits.

FIMS has been very useful for comparing fuel compositions, and for seeing the development of Fuel C deposit precursors at 130°C. Results with dodecane have been discouraging. The principal C₁₂ oxidation products, alcohols and hydroperoxides, fragment in the mass spectrometer and give similar peaks that overlap ketone peaks, probably in different proportions, so that the primary products and their subsequent changes have been hard to identify. The yields of dimeric and trimeric precursors have been surprisingly low. Further, the relative concentrations of different compounds in the same mixture and of the same compound in different mixtures depend on the evaporation before the FIMS is taken.

With enough oxygen, the coupling reaction² would be inhibited and the product would be unstable R_2O_2 . Hence gum and deposit formation may proceed best near the minimum oxygen concentration that permits oxidation. Some such measurements are important in the work proposed below.

We now need a sensitive, quantitative, and reproducible measure of accumulating deposit precursors under various experimental and storage conditions. We think that the inherent susceptibility of a fuel to deposit formation can be measured by the formation of nonvolatile materials in oxidations of fuels that have been freshly distilled in vacuum, with prompt examination of oxidized samples. The ASTM Test D2274-74 for soluble gum is not reproducible and we are trying to improve upon it. The problem is the very small but important amounts of nonvolatile compounds in small samples. We shall compare gum formation rates in several fuels and relate them to JFTOT and other tests. We shall then extend fuel stability studies to other pure hydrocarbons, their mixtures, and the effects of additives.

We shall examine by FIMS other hydrocarbons that may produce more dimer and trimer precursors than n-dodecane, possibly a sec-alkylbenzene, diethylbenzene, an alkylcyclohexane, and a tetralin derivative. We shall determine whether deposit precursors can be determined more usefully by our new gum test, light scattering, or gas and liquid chromatography, than by FIMS.

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